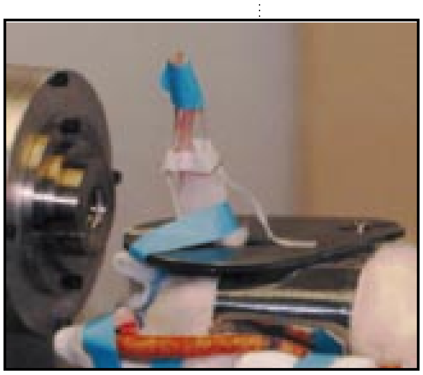
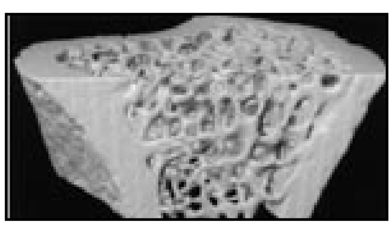
Chemistry and Materials Science

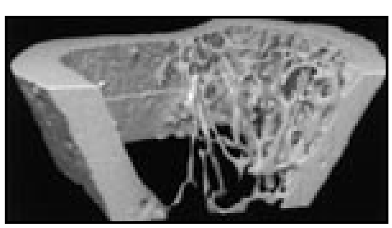
We continue to synthesize new materials, characterize their structure and properties, and evaluate their suitability for specific applications.

Chemistry and materials science is a field of study leading to applications that affect almost every aspect of our lives. We make direct contributions to each of the three major missions of the Laboratory, i.e., global security, global ecology, and the biosciences. Examples include science-based stockpile stewardship; U.S. economic competitiveness; the production of cleaner, cheaper energy; and cost-effective health-care projects. The Chemistry and Materials Science (C&MS) Directorate directly supports LLNL programs, performing both basic and applied research and development, and we also initiate leading-edge science and technology programs that will develop into major programs of the future.

An understanding of the field of chemistry and materials science is usefully viewed from the perspective of the steps by which new materials or processes are developed and then put to use. Thus, we view C&MS activities according to the methods we use in our research: (1) synthesis and processing of new materials, (2) characterization of the structure and properties of the materials, and (3) evaluation of material performance for specific applications. In each step, theory, modeling, and simulation provide essential guidance and feedback.







X-ray tomographic microscopy images of a live rat's femur. The lower image shows bone loss due to osteoporosis. At left, the rat is mounted on a goniometer stage variously positioned for the x-ray imaging detector to obtain cross-sectioned images for the 3D composites at right.

Our main activities in these areas are summarized below.

- **Materials Synthesis and Processing.** We are studying bicrystals, composites, advanced alloys, energetic materials, glasses and laser materials, lightweight porous materials, ceramics, electronic materials, coatings and surface modifications, nanoengineered materials, catalysts, chemical processing, surface physics and chemistry, aerogels, superplasticity, welding, and joining.
- **Characterization and Performance Evaluation.** We have core strengths in electron and probe microscopies, photoelectron spectroscopies, photon and neutron scattering, magnetism and transport, femtosecond spectroscopy, nuclear magnetic resonance (NMR) imaging, Mossbauer spectroscopy, mechanical and micro testing, ion-beam characterization, surface analytical techniques, mass spectroscopy, and trace analysis.
- **Theory, Simulation, and Modeling.** Our theoretical efforts involve materials by design, such as alloys, interfaces, heterogeneous materials, adhesives, molecular solids, and materials for microelectronics and opto-electronics. They also include molecular dynamics of surface processing, film growth, plasma processing, machining of metals and ceramics, transport phenomena, burn fronts and detonation, and equations of state (mathematical expressions that relate the volume of a material to pressure and temperature).

In the following sections, we highlight recent C&MS projects that incorporate important accomplishments made this year. These projects are multidisciplinary, cutting across the traditional boundaries of the scientific disciplines. Every project—be it primarily synthesis and processing; characterization and evaluation; or theory, simulation, and modeling—is inspired by one of our laboratory's major mission areas.

Studies with Synchrotron Radiation

The intense radiation that is generated when electrons are accelerated around a synchrotron enables the production of highly monochromatic, precisely tunable x-ray beams that can be used as a powerful diagnostic tool. This year, we used radiation from beam lines at the Stanford Synchrotron Radiation Laboratory and the Advanced Light Source (the premier facility for soft x-ray work at Lawrence Berkeley Laboratory) to study the near-neighbor arrangement of atoms in solids. To obtain details on atomic coordination and bonding in the solids, we used our new "quick" version of a measurement technique called extended x-ray atomic fine structure (EXAFS). This technique allows us to carry out the measurement in a few seconds, bringing us closer to the observation of material transformations in real time.

Our work with synchrotron radiation also allowed us to take the lead in developing photoelectron holography, an imaging technique that is loosely considered the electron analog to laser holography. Experimentally, photoelectron holography is the same as photoelectron diffraction (an effective tool for determining surface structure) except that the diffraction (interference) between the core-level electron measured directly from the photoemitter (the reference beam) and the same photoelectron wave that has scattered off neighboring atoms (the object wave) forms a true hologram. Thus, with photoelectron holography, we have successfully studied the detailed atomic structure of a buried interface. Because the core level from which the photoelectron is excited is very slightly altered by the electronic surroundings of the atom, we can selectively distinguish an atom at a buried interface from an identical atom one or more monolayers removed from the interface. This is made possible by the extremely high monochromatic selectivity possible with synchrotron radiation.

Another exciting development this year, also made possible by synchrotron radiation, was our study of x-ray diffraction of crystal structures in real time. We collected certain components of diffraction patterns in times as short as 100 ms. This technique allowed us to follow the rapid reaction sequences that occur in a combustion front during high-temperature synthesis of a material. We are now using it to characterize the rapid structural changes that occur in industrial welding. The results of this study will help us develop a better understanding of weldment microstructures and properties.

We also applied synchrotron radiation to the study of osteoporosis, a medical condition characterized by decreases in bone mass and density and the enlargement of bone spaces. Using microtomographic techniques developed within the chemistry and materials science directorate, we successfully probed the complicated composite structure of the femur of a rat, without harming

Highlights for 1994

- Developed a rapid, extended x-ray atomic fine structure technique to study atomic coordination and bonding in solids. The new technique allows us to carry out fine structure measurements in a few seconds, bringing us closer to observing material transformations in real time.

- Used photoelectron holography to study buried interfaces in solid-state materials. This was made possible by the extremely high monochromatic selectivity of synchrotron radiation.

- Collected certain components of diffraction patterns in times as short as 100 ms, allowing us to study the changes in crystal structures in near real time. This permits us to follow the rapid sequence of events that occur during industrial welding processes.

- Developed a new instrument that will enable us to diffusion-bond very flat, clean crystals in an ultrahigh vacuum (10^{-10} to 10^{-11} Torr) at up to 1500°C.

- Developed microtomographic techniques to probe the composite structure of a rat femur, without harming the rat, allowing us to follow and analyze the degeneration of bone structure in a single animal.

- Developed a very detailed understanding of the design and performance of reactive multilayers that could lead to a variety of industrial applications.

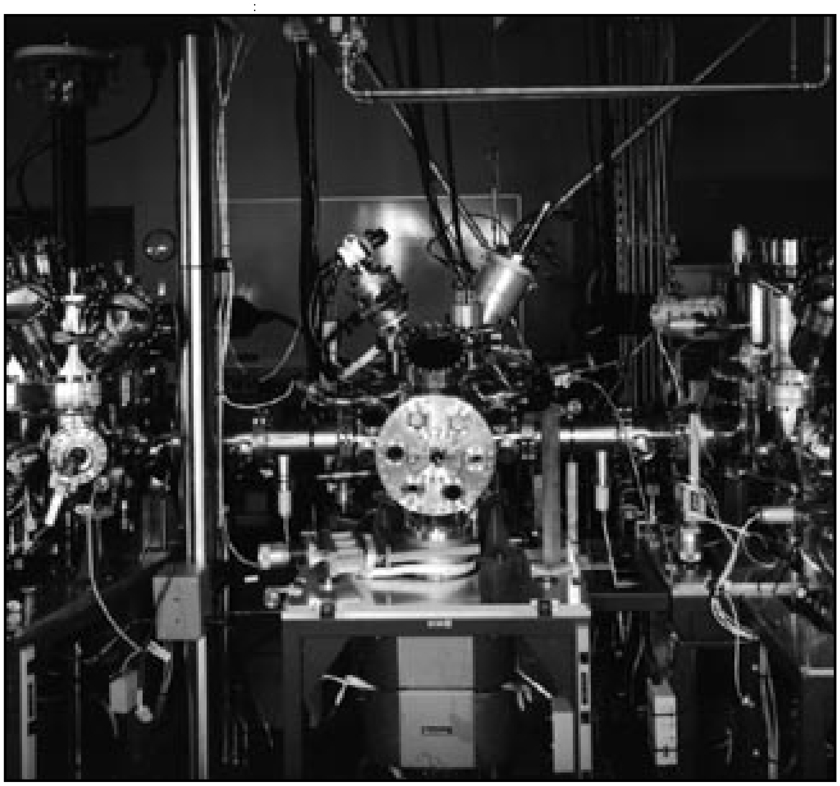
- Demonstrated the utility of aerogels in the deionization of aqueous solutions.

the animal. With this technology, the scientists and doctors collaborating on this project can continuously follow and analyze the degeneration of the bone structure in a single animal.

Interface Studies

The structure and strength of an interface—the region that forms the boundary between two materials—can have a major effect on the behavior of an engineered structure such as a bridge, aircraft, or integrated circuit. This relation is evident in the welded, brazed, and diffusion-bonded joints of structures. In addition, the behavior of an engineered structure is also affected by the properties of its materials, for example, the strength and ductility of its metals, alloys, or ceramics. These properties are determined by intrinsic properties of the material and also by its microstructure, which is in turn influenced by an interface—in this case, the boundary between two individual grains, or crystals.

The ultrahigh vacuum diffusion-bonding machine.



One fundamental problem associated with understanding and predicting interface properties is that we cannot accurately fabricate, characterize, and modify the composition and atomic structure of an interface. This year, we took an important step in addressing the issue by completing the development of a new instrument called the ultrahigh vacuum diffusion-bonding machine. Although we designed this machine as the next generation of a similar machine located in Germany, it is unique in its own right. It will enable us to diffusion bond, in an ultrahigh vacuum (10^{-10} to 10^{-11} Torr) at up to 1500°C, very flat (to tens of nanometers), clean crystals aligned to a precision of 0.2 deg. Eventually, we will also be able to carry out controlled doping of interfaces to simulate the effects of grain boundary segregation in real metals and alloys.

We have used this instrument to study the atomic structure of grain boundaries in niobium metal. We constructed interfaces of known symmetry and orientation and then experimentally characterized the atomic arrangement at the interface using a high-resolution transmission electron microscope capable of resolving individual atomic positions. This information has allowed us to distinguish the relative validity of two widely used theoretical approaches. We also used the facility to characterize the detailed failure mechanism of an aluminum/aluminum oxide joint, which provided us our first experience with a joining problem at an interface. We expect this facility to enable us to achieve other breakthroughs in the science of interface behavior.

Waste Management Technologies

In support of the Laboratory's waste management efforts, we are participating in the investigation of three different technologies that could be used to destroy organic wastes in the Mixed Waste Management Facility: mediated electrochemical oxidation, UV/H_2O_2 (ultraviolet hydrogen peroxide) oxidation, and molten salt pyrolysis. Our responsibility is to provide the analytical measurements to support bench testing of the processes for each technology under consideration. We are measuring total inorganic and total organic carbon to measure process efficiency and characterizing residual and breakdown products of UV/H_2O_2 oxidation of chlorinated hydrocarbons, such as trichloroethylene.

In addition to our work in waste management, we operate a state-certified laboratory to assist in all aspects of managing hazardous waste that is generated on-site.

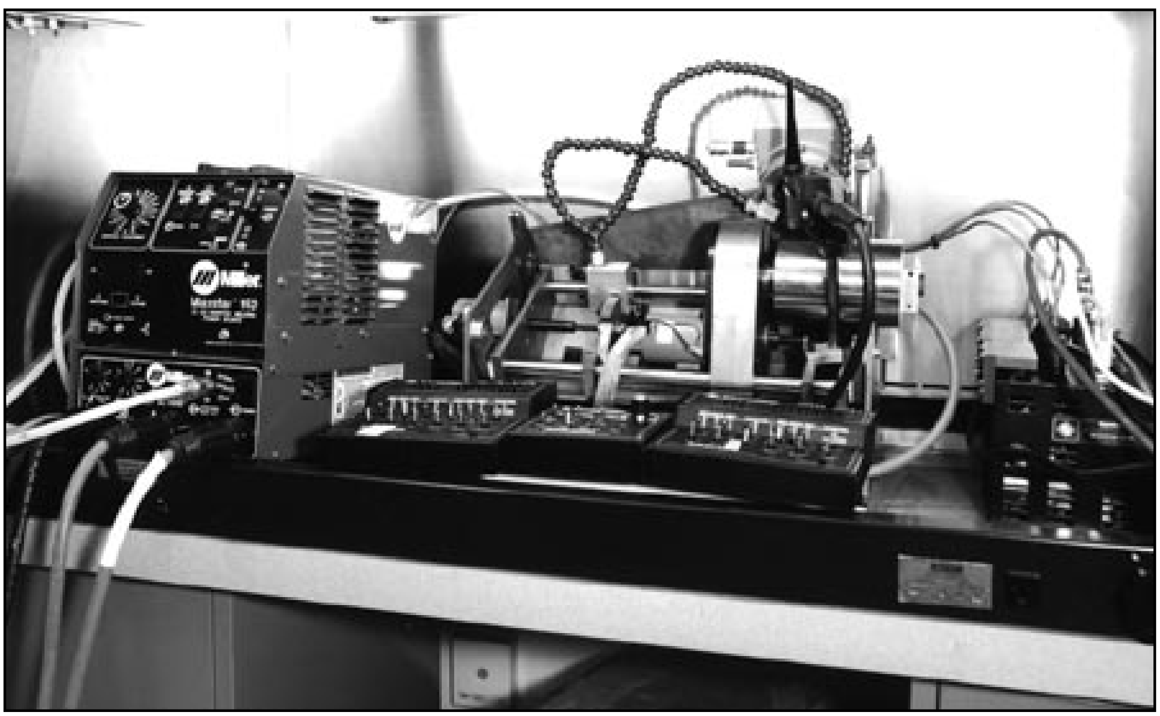
Sensing and Detecting Methods

To support the Laboratory's efforts in nonproliferation, arms control, and intelligence, we are developing highly sensitive and specific methods for detecting chemical warfare agent precursors and hydrolysis products and seeking new ways to miniaturize instruments for field use. For example, we are developing an aircraft-mountable, time-of-flight mass spectrometer for real-time identification of volatile airborne solvents and a laser-spectroscopy-based method for remote sensing of effluent plumes, such as those that might escape from a chemical processing plant. This work is closely associated with the work we are doing for the Treaty Verification Program, i.e., to develop sampling kits for on-site detection of nuclear weapon capabilities.

We are also supporting the Laboratory's evolving mission in biomaterials and health care by developing new instrumentation for mass spectrometry. This instrumentation will be used in mass spectrometric analyses of large, biological molecules.

Characterizing Laser Materials

In support of Nova and the National Ignition Facility, we are characterizing the materials used in



We are characterizing the rapid structural changes that occur during industrial welding with spatially resolved x-ray diffraction. This photo includes the LLNL-developed system, which can be used with most any synchrotron source x-ray beam.

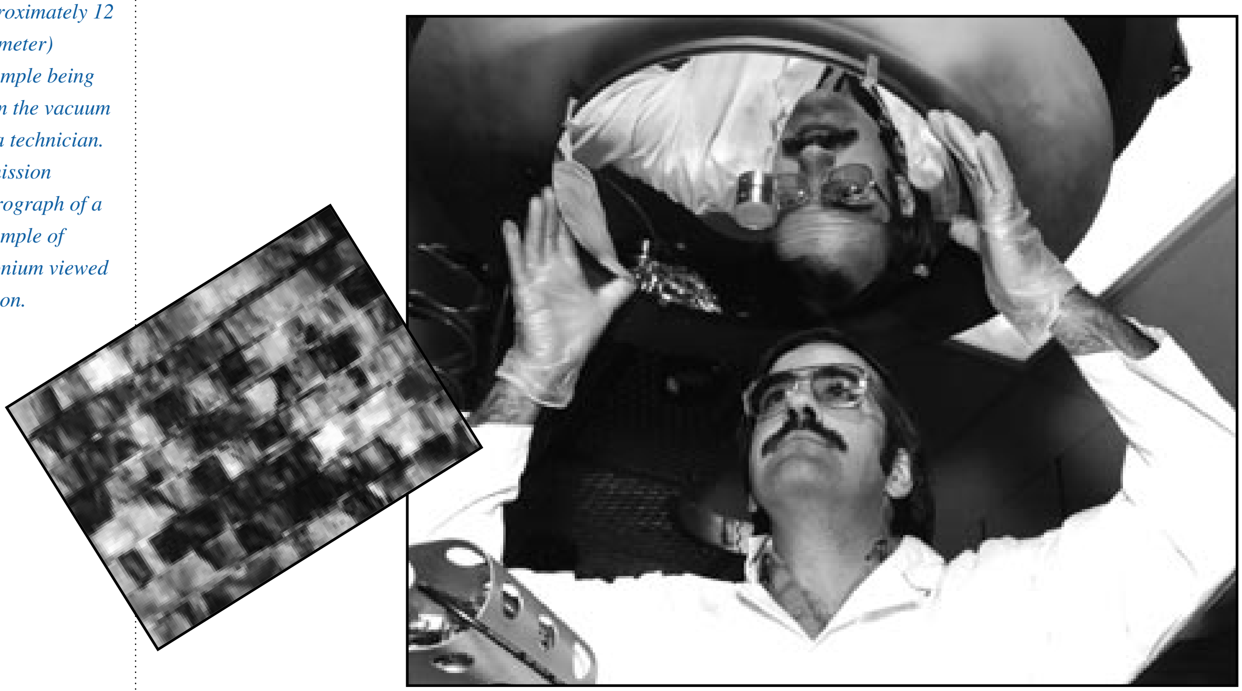
nonlinear optical components, such as potassium dihydrogen phosphate (KDP). We are developing methods for determining trace metal impurities and using nuclear magnetic resonance spectroscopy to measure the deuteration levels. In the realm of target fabrication, we provide detailed analyses of the gases in an ICF target and of the helium in the Nova laser's line-of-sight. We determine the purity of the laser dyes and solvents used by laser program personnel. We assess separator performance in the uranium-atomic vapor laser isotope separation process by measuring the elemental and isotopic compositions of the material deposited during the process as a function of location in the separator.

Nanostructured Materials

The demand for better performance from materials has resulted in new methods of synthesizing materials in a novel structure. One way to structure a material is to take advantage of properties that arise from specific material features at the nanometer scale, such as those found in multilayers and aerogels.

We refer to multilayers as nanoengineered materials because we construct them atom by atom with a predetermined arrangement and goal in mind. This is a radical departure from classical material synthesis, sometimes referred to as "ingot metallurgy," where, for the most part, we accept the atomic arrangement dictated by nature and manipulate properties through the optimization of microstructure. Multilayer synthesis allows us to prepare metastable arrangements of atoms that are unobtainable by other means and that possess unusual and outstanding properties.

Our most important recent advance in multilayer synthesis has been our ability to prepare dielectric layers with carefully and reproducibly controlled atomic structure and composition. This is important in current industrial applications associated with aircraft engine development, and it also opens a new realm of applications. For example, we are exploring the fabrication of high-voltage



A large (approximately 12 inches in diameter) multilayer sample being removed from the vacuum chamber by a technician. Inset: transmission electron micrograph of a multilayer sample of copper–zirconium viewed in cross section.

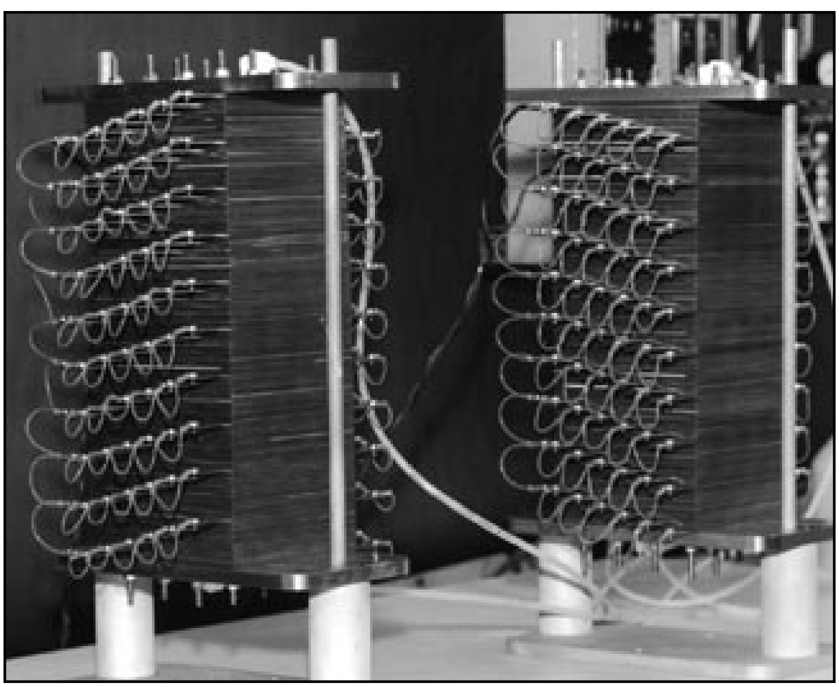
capacitors with unprecedented energy storage and very rapid energy delivery. We have also explored the fabrication of reactive multilayers—materials whose stored energy may exceed that of high explosives but is released in milliseconds rather than microseconds without the production of a shock wave. In the last year, this work led to a very detailed understanding of the design and performance of these materials and a strong expectation of important future industrial applications.

Aerogels, unlike multilayers, provide a wide range of unusual properties associated with a specific nanostructural arrangement. In the past year, we have taken advantage of these properties to demonstrate the utility of these unique materials in the deionization of aqueous solutions. We have developed an aerogel-based unit with a tremendous capacity for removing ions from aqueous solution (as in desalinization). This unit consumes only a fraction of the electric power required by conventional approaches, and it is easily regenerated by reversing the potential.

Summary

Our work in chemistry and materials science exemplifies disciplinary research and programmatic support. The disciplinary research is intended to sharpen the skills of our scientists, advance the frontiers of scientific knowledge, and provide the seeds for programs of the future. The programmatic support provides the very best scientific and engineering talent for Laboratory programs and offers the potential for new program areas. We are convinced that chemistry and materials science will be key to the future success of the Laboratory whatever its mission, and we are firmly committed to supporting this mission with the very best in scientific talent.

For further information contact Jeffrey Wadsworth (510) 423-2184 or Lawrence R. Newkirk (510) 422-5476.



Prototype aerogel system for the deionization of aqueous solutions. It is based on multiple cells containing carbon aerogel as the active component.